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I, Japanese Patent Attorney Yoshitaka OSHIDA, having my office at GINZA BULDING 3-12, 3-CHOME, GINZA CHUO-KU, TOKYO, JAPAN, do solemnly and sincerely declare:

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2. That the attached document: Specification

is a true translation into the English language.

And I make this solemn declaration conscientiously believing the same to be true and correct.

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平成１６年登簿第　1000　号

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平成１６年　５月　１３日

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(Convention de La Haye du 5 octobre 1961)

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This is to certify that the annexed is a true copy of the following application as filed with this office.

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Applicant(s): NEOMAX CO.,LTD.

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Commissioner, Japan Patent Office: Yasuo IMAI

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【Name of Document】 Specification

【Title of Invention】 THERMOELECTRIC CONVERSION MATERIAL AND THERMOELECTRIC CONVERSION ELEMENT

【What is claimed is】

【Claim 1】 A thermoelectric conversion material having a crystal structure in which at least one of germanium, carbon and tin in an amount of 5 to 10 at% and at least one type of added elements to make a p-type or n-type semiconductor in an amount of 0.001 to 20 at% are contained in silicon, and one or more of said germanium, carbon and tin or further one or more types of added elements are deposited at the grain boundary portion of a polycrystalline silicon.

【Claim 2】 A thermoelectric conversion material having a crystal structure in which at least one of germanium, carbon and tin in an amount of 5 to 10 at%, at least one type of added elements to make a p-type or n-type semiconductor in an amount of 0.001 to 20 at%, and one or more types of Group III-V compound semiconductors or Group II-VI compound semiconductors in an amount of 1 to 10 at% are contained in silicon, and one or more of said germanium, carbon and tin or further one or more types of added elements are deposited at the grain boundary portion of a polycrystalline silicon.

【Claim 3】 The thermoelectric conversion material according to claim 1 or 2, wherein the material consists of

a p-type or n-type semiconductor whose carrier concentration is 10^{17} to 10^{21} (M/m^3) and whose thermal conductivity is 50 W/m·K or less.

【Claim 4】 A thermoelectric conversion element having a crystal structure in which at least one of germanium, carbon and tin in an amount of 5 to 10 at% and at least one type of added elements to make a p-type or n-type semiconductor in an amount of 0.001 to 20 at% are contained in silicon, and one or more of said germanium, carbon and tin or further one or more types of added elements are deposited at the grain boundary portion of a polycrystalline silicon, in which a p-n junction of a p-type silicon semiconductor and an n-type silicon semiconductor is formed on their one end sides.

【Claim 5】 A thermoelectric conversion element having a crystal structure in which at least one of germanium, carbon and tin in an amount of 5 to 10 at%, at least one type of added elements to make a p-type or n-type semiconductor in an amount of 0.001 to 20 at%, and one or more types of Group Ⅲ-Ⅴ compound semiconductors or Group Ⅱ-Ⅵ compound semiconductors in an amount of 1 to 10 at% are contained in silicon, and one or more of said germanium, carbon and tin or further one or more types of added elements are deposited at the grain boundary portion of a polycrystalline silicon, in which a p-n junction of a p-type silicon semiconductor and an n-type silicon

semiconductor is formed on their one end sides.

【Claim 6】 The thermoelectric conversion element according to claim 4 or 5, wherein the material consists of a p-type or n-type semiconductor whose carrier concentration is 10^{17} to 10^{21} (M/m^3) and whose thermal conductivity is 50 W/m・K or less.

【Detailed Description of the Invention】

【0001】

【Technical Field of the Invention】

This invention relates to a novel thermoelectric conversion material in which one or more of germanuium, carbon and tin and various types of added elements are contained in silicon in an amount of 30 at% or less, in total, and more particularly relates to a polycrystal silicon-based thermoelectric conversion material, characterized in that by making a structure in which an added element-rich phase is dispersed in the grain boundary of a silicon-rich phase composed chiefly of silicon, a Seebeck coefficient is extremely large, the thermal conductivity becomes low, 50 W/m・K or less, allowing the thermoelectric conversion efficiency to be raised dramatically, and because of a silicon chiefly contained, which is an abundant resource, the environmental pollution is extremely little.

【0002】

【Background Art】

In the reports of J. P. Dismukes et al. (J. Appl. Phys., 35(1964)2899.) and N. Kh. Abrikosov et al. (Sov. Phys. -Semicon., 2(1969)1468.), it is known that the thermal conductivity can be lowered by adding germanium to silicon, by which the Figure of merit is improved.

【0003】

This silicon-germanium has a state in which there is a broad liquidus and solidus for complete solid solution, and silicon and germanium tend to segregate. Further, since the raw material cost of germanium is high, it has not found widespread use.

【0004】

On the other hand, as a thermoelectric conversion material with good productivity, stable quality and low price, the inventors proposed a silicon-based thermoelectric conversion material with an extremely large Seebeck coefficient and a dramatically enhanced thermoelectric conversion efficiency, for example, by adjusting the addition of one or more types of various added elements such as phosphorus, boron and aluminum and the added amount such that the carrier concentration in a silicon semiconductor is 10^{17} to 10^{21} (M/m^3)(W099/22410).

【0005】

【Problems to be solved by the Invention】

This silicon-based material can decrease the thermal conductivity by various added elements. Further, at a

given carrier concentration, Seebeck coefficient is equivalent to or better than that of the conventionally known Si-Ge-based and Fe-Si-based material, and this material exhibits a good Figure of merit as a thermoelectric conversion material and can obtain a high performance.

【0006】

Generally, the thermal conductivity (κ) is given by a sum of the conduction (κel) due to a carrier (free electron) and the conduction (κph) due to phonon. Since in the semiconductor region (carrier concentration < 10^{21} (M/m^3)) the conduction due to phonon is dominant, it is necessary to increase the scattering of phonon in order to decrease the thermal conductivity. For this, it is effective to add impurity elements in silicon.

【0007】

However, if a Group II, Group III, Group V, Group VI element, a transition metal element, or a rare earth element is added in silicon, a carrier is generated in silicon. The carrier concentration that is effective for a thermoelectric conversion material is 10^{17} to 10^{21} (M/m^3), and there is a limit to the added amount, wherease the thermal conductivity of the silicon-based material must be further decreased in order to raise the Figure of merit of the thermoelectric conversion material.

【0008】

An object of this invention is to provide a silicon-based thermoelectric conversion material and thermoelectric conversion element in which the thermal conductivity of the material could be greatly decreased and the Figure of merit markedly improved without lowering the Seebeck coefficient or electrical conductivityy of the silicon-based thermoelectric conversion material.

【0009】

【Means to solve the Problems】

Relating to the decrease of the thermal conductivity of silicon-based thermoelectric conversion material, the inventors looked into compositions and, as the results, noted that in the Group Ⅳ element (germanium, carbon and tin) which is the same as a silicon, there is no carrier generation, and if the added amount is small, the germanium is replaced with silicon, resulting in a diamond-like crystal structure, and furthermore the phonon scattering is greater because the atomic weight of germanium is different from that of silicon, allowing the thermal conductivity to be greatly lowered.

【0010】

The inventors found that by adding carbon, germanium and tin, the thermal conductivity can be decreased largely without changing the carrier concentration in a silicon-based material, and, as the result of further investigation, found that when the above-mentioned Group Ⅳ element is

added, the thermal conductivity decreases sharply up to an added amount of 5 at%, and more or less reaches saturation at 10 at%, so an added amount of 5 to 10 at% is ideal for lowering the thermal conductivity, and furthermore, the structure must be such that the Group IV element is deposited at the grain boundary portion of the polycrystal silicon.

【0011】

That is, this invention provides a thermoelectric conversion material having a crystal structure in which at least one of germanium, carbon and tin in an amount of 5 to 10 at% and at least one type of added elements to make a p-type or n-type semiconductor in an amount of 0.001 to 20 at%, or one or more types of Group III-V compound semiconductors or Group II-VI compound semiconductors in an amount of 1 to 10 at% are contained in silicon, and one or more of said germanium, carbon and tin or further one or more types of added elements are deposited at the grain boundary portion of a polycrystalline silicon.

【0012】

According to the thermoelectric conversion material of the present invention, by such a structure, a p-type or n-type semiconductor whose carrier concentration is 10^{17} to 10^{21} (M/m^3) and whose thermal conductivity is 50 W/m・K or less can be obtained. Accordingly, it becomes possible to manufacture a thermoelectric conversion element forming a p-

n junction of a p-type silicon semiconductor and an n-type silicon semiconductor on their one end sides.

【0013】

【Mode of Working of the Invention】

The crystal structure, a characteristic of the thermoelectric conversion material of the present invention will be described below. The structure is a structure which is basically a polycrystal silicon, and in which an added element is contained within each crystal grain, but almost all is silicon, and one or more of germanium, carbon and tin, and an added element are simultaneously deposited at the grain boundary portion of the silicon crystal grain, which means conveniently a structure formed by a silicon-rich phase in which silicon occupies 80 at% or more and an added element-rich phase occupied by one or more of germanium, carbon, and tin, or further one or more types of added elements at the half or more.

【0014】

The inventors produced $Si_{100-x}Ge_x$ melts by arc melting, with various added amounts of germanium (4N) into high purity silicon (10N), and quenched at a cooling rate of 50 to 200K/sec after melting to produce sample substrates. The crystal structure was observed by EPMA. Fig. 1A shows an EPMA photograph observing only germanium when x = 5 and Fig. 2A is when x = 10. The black parts in the photographs are the silicon-rich phase, which is virtually all silicon,

although a trace amount of added element is included, and the white parts are the added element germanium-rich phase, and it can be seen that in this structure the germanium-rich phase is formed or dispersed at the grain boundary of the silicon-rich phase.

【0015】

Also, a phosphorus was added to the above-mentioned $Si_{100-x}Ge_x$ melts, but when just the phosphorus was observed, the EPMA photographs were as shown in Figures 1B and 2B, with the white parts indicating places where the doped phosphorus is present, and it can be seen that in this structure the phosphorus is segregated in the same locations where the germanium-rich phase in Figures 1A and 2A as mentioned above was formed at the grain boundary of the silicon-rich phase.

【0016】

Meanwhile, as shown in Figures 3A and 3B, which are EPMA photographs of just germanium when x = 15 with the above-mentioned $Si_{100-x}Ge_x$ melts and just phosphorus, respectively, the overall structure becomes an alloy phase in which the silicon and germanium are in solid solution, and it is clear that this is completely different from the structure of the thermoelectric conversion material pertaining to the present invention.

【0017】

In other words, the structure of the thermoelectric

conversion material of the present invention is a structure in which are formed a silicon-rich phase consisting of silicon alone or almost entirely of silicon but including a trace amount of added element, and an added element-rich phase in which one or more of germanium, carbon, tin or an added element is segregated at the grain boundary of this silicon-rich phase. The size of the silicon-rich phase varies with the cooling rate, but is about 10 to 500 μm.

【0018】

The relationship between carrier concentration and the state of crystal grain boundary deposition of an added element of carbon or tin, or phosphorus or boron was examined, which confirmed that the carrier concentration obtained from the added amount was in fairly good agreement with the measured carrier concentration. Because of the structure in which Group IV element and the added element-rich phase were formed at the grain boundary of the silicon-rich phase, the added element was clumped at the crystal grain boundary, the electrical conductivity resulting from carriers was high, a high Seebeck coefficient was obtained in the silicon-rich phase within the crystal grains, and most importantly the thermal conductivity was reduced to 50 W/m・K or less.

【0019】

With a thermoelectric conversion material of the present invention, thermal conductivity will be high if one

or more of germanium, carbon, and tin are contained in an amount less than 5 at%, so a high Figure of merit will not be obtained, but while thermal conductivity will decrease somewhat if 10 at% is exceeded, the Group IV element will at the same time also diffuse into the silicon-rich phase in the particles, producing a solid solution, so there will be a drop in the high Seebeck coefficient of the silicon, and the Figure of merit will be lower. Thus, the Group IV elements other than silicon should be contained in an amount of 5 to 10 at%.

【0020】

In the present invention, the purpose of adding a Group III－V compound semiconductor or a Group II－VI compound semiconductor is to reduce thermal conductivity without changing the carrier concentration of the material, and the desired effect will not be obtained below 1 at%, but adding in an amount over 10 at% will result in almost no decrease in thermal conductivity, so an amount of 1 to 10 at% is preferable.

【0021】

In this invention, added elements to make a p-type or n-type semiconductor decrease the thermal conductivity at the carrier concentration within the required range and at the same time are added to obtain a high Seebeck coefficient. When the applications of a thermoelectric conversion material are considered, emphasis must be placed

on one of the characteristics, such as the Seebeck coefficient, electrical conductivity, or thermal conductivity depending on the conditions which vary with the application, such as the heat source, where and how the material is used, and the size of the current and voltage to be handled, but the thermoelectric conversion material of the present invention allows the carrier concentration to be determined by means of the added amount of the selected added element. Any added element can be used, and one or more of them may be contained within a range from 0.001 to 20 at%.

【0022】

It is preferable for the added elements for creating a p-type semiconductor to be one or more types selected from each group of a group A (Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, B, Al, Ga, In, Tl) and transition metal elements M_1 (Y, Mo, Zr).

【0023】

It is preferable for the added elements for creating an n-type semiconductor to be one or more types selected from each group of a group B (N, P, As, Sb, Bi, O, S, Se, Te), transition metal elements M_2 (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt, Au; where Fe accounts for 10 at% or less), and rare earth elements RE (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu).

【0024】

In this invention, by adding at least one type of each of Group IV element and Group V element and controlling the carrier concentration to 10^{19} to 10^{21} (M/m^3), it is possible to increase phonon scattering without changeing the carrier concentration and to decrease the thermal conductivity. Further, a p-type semiconductor will be obtained if the Group III element is contained in an amount 0.3 to 5 at% larger than the Group V element, and an n-type semiconductor will be obtained if the Group V element is contained in an amount 0.3 to 5 at% larger than the Group III element.

【0025】

With the silicon-based thermoelectric conversion material of the present invention, the above-mentioned structure is obtained by cooling a silicon-based molten material, and arc melting and high-frequency melting are ideal melting methods for mass production. The cooling rate of the silicon-based molten material is suitably determined by the type and combination of added elements (discussed below), the added amount, and so forth, as well as the cooling method employed, and the form such as an ingot, a thin sheet, a substrate, or a ribbon.

【0026】

Cooling methods that can be employed in the present invention include cooling the ingot just as it is, and cooling while pulling, such as a method in which a known

Czochralski (CZ) or floating zone (FZ) method for obtaining monocrystalline silicon is utilized and pulling and cooling are performed under conditions that allow polycrystalline silicon to be obtained. Because a CZ or FZ method allows numerous substrates of the required thickness to be manufactured from a pulled ingot rod, they are ideal methods for manufacturing a silicon-based substrate for use in thermoelectric conversion elements. Manufacture by a zone leveling (ZL) method is also possible.

【0027】

Other methods may also be employed, such as a method in which a thin sheet is fabricated by casting and cooling a silicon-based molten material in a shallow plate, or utilizing a roll cooling method such as a known melt quenching method to control the cooling rate so that a thin sheet of the required thickness will be obtained.

【0028】

For instance, when a silicon-based molten material is cast and cooled in a shallow plate, or the plate is water-cooled or brought into contact with a chiller, then cooling at a rate of at least 50K/sec is appropriate, for example, which will keep the crystal grain size to just a few hundred microns or less and result in a high Seebeck coefficient. A preferable cooling rate is 50K/sec to 500K/sec, and it is possible to achieve an average crystal grain size of 10 to 500 μm.

【0029】

Even if the silicon-based thermoelectric conversion material according to the present application is a sintered body, a structure in which an added element-rich phase of germanium or the like is dispersively formed at the grain boundary of a silicon-rich phase is formed through the segregation of the added element in solid solution in the raw material powder particles during sintering. It is also effective for the sintering powder itself to have the same crystal structure. This can be obtained by the controlling of the cooling rate after casting, the crystal grain size is controlled to relatively small by quenching and the suitable segregation of the added elements other than silicon occurs in the crystal grain boundary, by which inspite of a high electrical conductivity materials and powders showing a high Seebeck coefficient can be obtained, and further by sintering using these powders, the segregation of the added elements during sintering becomes more easy and effective to obtain a silicon-based thermoelectric conversion material of a sintered body having a high Seebeck coefficient.

【0030】

According to the manufacturing method of the raw material powder for a sintered body, it is possible to manufacture by pulverizing the materials due to various melting methods as mentioned above. Further, in order to

obtain a silicon or a silicon-based powder, it is possible to manufacture a ribbon by a roll cooling method such as melt quenching for pulverization, or to obtain directly a powder by a spray method such as gas atomization, each allowing for a fine crystal grain size of 1 to 50 μm and making it possible to lower the thermal conductivity.

【0031】

Further, it is possible to melt a pure silicon raw material or a silicon-based melting raw material of the required composition by an arc melting or high-frequency melting method, to adhere added elements to the surface of a silicon or a silicon-based powdery grain of the required grain size obtained by pulverizing the cast ingots or thin sheet, and to sinter it.

【0032】

As a method of coating the added element onto the surface of a silicon powder or a silicon powder containing an added element, any known growth, film formation, binding, or adhesive means, for example, a known vapor phase growth method such as vapor deposition, sputtering, CVD, discharge plasma treatment, or plasma treatment using a gas containing an added element can be used. Further, a method of embedding an added element on the surface of a silicon powder by mechanofusion treatment can be also adopted.

【0033】

In order to manufacture a thermoelectric conversion

element, p-type and n-type semiconductors are made using a thermoelectric conversion material of various compositions as mentioned, the p-n junction of them is performed and an element of the required shape is formed. For example, it is possible to make it by sintering a pair of a p-type semiconductor and an n-type semiconductor formed intergrally in the required shape powder-metallurgically, and directly performing a p-n junction.

【0034】

【Examples】

Example 1

In order to produce a p-type silicon-based thermoelectric semiconductor, high-purity silicon (10N), a Group Ⅳ element (germanium, carbon, or tin), and a Group Ⅲ element were compounded as shown in Table 1, after which they were arc melted in an argon gas atmosphere. The button-shaped ingots thus obtained were cut to sizes of 5 × 5 × 15 mm, 10 × 10 × 2 mm, and 10 (diameter) × 2 mm, and the Seebeck coefficient (S), Hall coefficient (including the carrier concentration (n) and electrical conductivity (ρ)), and thermal conductivity (κ) were measured for each.

【0035】

The temperature differential between the high and low temperature portions was set to 6℃, the thermoelectromotive force of the p-type semiconductors in

which the average temperature between the high and low temperature portions was 200℃ was measured with a digital multimeter, and this value was divided by the temperature differential (6℃) to find the Seebeck coefficient. The Hall coefficient was measured by applying an AC magnetic field of 0.4T at 200℃, and the electrical resistance was measured by four-terminal method simultaneously with the carrier concentration. The thermal conductivity was measured at 200℃ by laser flash method.

【0036】

Tables 1 and 2 show the obtained measurement values and the Figure of merit ($Z = S^2/\rho\kappa$). The measurement values of an Si-Ge alloy (containing 30 at% germanium) and of silicon not doped with germanium are also shown as comparative examples.

【0037】

Example 2

In order to produce an n-type silicon-based thermoelectric semiconductor, high-purity silicon (10N), a Group IV element (germanium, carbon, or tin), and a Group V element were compounded as shown in Table 2, after which they were arc melted in an argon gas atmosphere. The button-shaped ingots thus obtained were cut to sizes of 5 × 5 × 5 mm, 10 × 10 × 2 mm, and 10 (diameter) × 2 mm.

【0038】

The Seebeck coefficient (S), Hall coefficient

(including the carrier concentration (n) and electrical conductivity (ρ)), and thermal conductivity (κ) were measured for each in the same manner as in Example 1. Tables 3 and 4 show the obtained measurement values and the Figure of merit ($Z = S^2/\rho\kappa$). As a comparative material, measurement values are also given for an Si-Ge alloy (30 at% germanium) and silicon to which no germanium was added.

【0039】

Example 3

In order to produce p- and n-type silicon-based thermoelectric semiconductors, high-purity silicon (10N), a Group IV element (germanium, carbon, or tin), a Group III-V compound semiconductor (GaP, GsP) or a Group II-VI compound semiconductor (ZnS), and a Group II element or Group III element, or a Group V element or Group VI element, which is a dopant, were compounded as shown in Table 3, after which they were melted in a high-frequency melting furnace in a 300 mmHg argon gas atmosphere.

【0040】

The ingots thus obtained were cut to sizes of 5 × 5 × 5 mm, 10 × 10 × 2 mm, and 10 (diameter) × 2 mm. The Seebeck coefficient (S), Hall coefficient (including the carrier concentration (n) and electrical conductivity (ρ)), and thermal conductivity (κ) were measured for each. Tables 5 and 6 show the obtained measurement values and the Figure of merit ($Z = S^2/\rho\kappa$). As a comparative material,

measurement values are also given for an Si-Ge alloy (6.5 at% germanium) to which no Group Ⅲ - Ⅴ compound semiconductor or Group Ⅱ - Ⅵ compound semiconductor was added.

【0041】

【Table 1】

	No.	Matrix	Added element		Added element		Carrier concentration $n(M/m^3)$
			Element name	Added amount (at%)	Element name	Added amount (at%)	
Example	1	Si	Ge	5	B	0.3	$1.82\times10^{+20}$
	2	Si	Ge	6.5	B	0.3	$1.78\times10^{+20}$
	3	Si	Ge	8	Al	0.3	$1.65\times10^{+20}$
	4	Si	Ge	10	B	0.3	$1.68\times10^{+20}$
	5	Si	Ge	10	B+Al	3+5	$4.71\times10^{+20}$
	6	Si	C	6.5	B	0.3	$1.72\times10^{+20}$
	7	Si	C	8	Al	0.3	$1.77\times10^{+20}$
	8	Si	Sn	6.5	B	0.3	$1.62\times10^{+20}$
Comparative Example	9	Si	Ge	3	B	0.3	$1.90\times10^{+20}$
	10	Si	Ge	12	B	0.3	$1.65\times10^{+20}$
	11	Si	Ge	20	B	0.3	$1.54\times10^{+20}$
	12	Si	Ge	30	B	0.3	$1.59\times10^{+20}$
	13	Si	–	–	B	0.3	$2.00\times10^{+20}$

【0042】

【Table 2】

	No.	Thermoelectric characteristics			
		Seebeck coefficient S(mV/K)	Electrical resistance ρ ($\Omega \cdot$ m)	Thermal conductivity κ (W/m · K)	Figure of merit (/K)
Example	1	0.30	7.70×10^{-6}	8.2	1.4×10^{-3}
	2	0.32	7.90×10^{-6}	7.6	1.7×10^{-3}
	3	0.34	8.10×10^{-6}	7.2	2.0×10^{-3}
	4	0.33	8.30×10^{-6}	6.8	1.9×10^{-3}
	5	0.20	4.20×10^{-6}	5.3	1.8×10^{-3}
	6	0.27	6.90×10^{-6}	10.0	1.1×10^{-3}
	7	0.26	7.40×10^{-6}	8.5	1.1×10^{-3}
	8	0.29	8.20×10^{-6}	10.9	9.4×10^{-4}
Comparative Example	9	0.29	7.60×10^{-6}	14.0	7.9×10^{-4}
	10	0.26	9.40×10^{-6}	6.8	1.0×10^{-3}
	11	0.24	9.90×10^{-6}	6.6	8.8×10^{-4}
	12	0.22	8.70×10^{-6}	6.3	8.8×10^{-4}
	13	0.33	7.30×10^{-6}	65.0	2.3×10^{-4}

【0043】

【Table 3】

	No.	Matrix	Added element		Added element		Carrier concentration n(M/m³)
			Element name	Added amount (at%)	Element name	Added amount (at%)	
Example	21	Si	Ge	5	P	1.0	$1.92 \times 10^{+20}$
	22	Si	Ge	6.5	P	1.0	$1.84 \times 10^{+20}$
	23	Si	Ge	8	As	1.0	$1.69 \times 10^{+20}$
	24	Si	Ge	10	P	1.0	$1.73 \times 10^{+20}$
	25	Si	Ge	10	P+Sb	3.0+5.0	$4.01 \times 10^{+20}$
	26	Si	C	6.5	P	1.0	$1.85 \times 10^{+20}$
	27	Si	C	8	Bi	1.0	$1.76 \times 10^{+20}$
	28	Si	Sn	6.5	P	1.0	$1.82 \times 10^{+20}$
Comparative Example	29	Si	Ge	3	P	1.0	$1.98 \times 10^{+20}$
	30	Si	Ge	12	P	1.0	$1.67 \times 10^{+20}$
	31	Si	Ge	20	P	1.0	$1.61 \times 10^{+20}$
	32	Si	Ge	30	P	1.0	$1.62 \times 10^{+20}$
	33	Si	–	–	P	1.0	$2.08 \times 10^{+20}$

【0044】

【Table 4】

	No.	Thermoelectric characteristics			
		Seebeck coefficient S(mV/K)	Electrical resistance $\rho(\Omega \cdot m)$	Thermal conductivity κ (W/m · K)	Figure of merit (/K)
Example	21	−0.31	7.90×10^{-6}	9.3	1.3×10^{-4}
	22	−0.34	8.20×10^{-6}	8.2	1.7×10^{-3}
	23	−0.37	8.40×10^{-6}	7.5	2.2×10^{-3}
	24	−0.35	8.60×10^{-6}	7.0	2.0×10^{-3}
	25	−0.24	3.90×10^{-6}	6.3	2.3×10^{-3}
	26	−0.29	7.20×10^{-6}	10.6	1.1×10^{-3}
	27	−0.30	7.70×10^{-6}	8.8	1.3×10^{-3}
	28	−0.31	8.20×10^{-6}	11.2	1.0×10^{-3}
Comparative Example	29	−0.31	7.90×10^{-6}	13.2	9.2×10^{-4}
	30	−0.27	1.02×10^{-5}	6.9	1.0×10^{-3}
	31	−0.25	1.04×10^{-5}	6.7	9.0×10^{-4}
	32	−0.24	9.00×10^{-6}	6.5	9.8×10^{-4}
	33	−0.35	7.80×10^{-6}	58.0	2.7×10^{-4}

【0045】

【Table 5】

	No.	Matrix	Added element		Added element		Added element		Carrier Concentration n(M/m³)
			Element name	Added amount (at%)	Element name	Added amount (at%)	Element name	Added amount (at%)	
Example	41	Si	Ge	6.5	GaP	3.0	B	0.6	$1.87\times10^{+20}$
	42	Si	Ge	6.5	GaP	3.0	P	1.0	$2.01\times10^{+20}$
	43	Si	Ge	6.5	GaP	5.0	B	0.6	$1.84\times10^{+20}$
	44	Si	Ge	6.5	GaP	5.0	P	1.0	$2.03\times10^{+20}$
	45	Si	Ge	6.5	GaAs	3.0	Al	0.6	$1.85\times10^{+20}$
	46	Si	Ge	6.5	GaAs	3.0	As	1.0	$1.99\times10^{+20}$
	47	Si	Ge	6.5	ZnS	3.0	Be	0.3	$1.79\times10^{+20}$
	48	Si	Ge	6.5	ZnS	3.0	S	1.0	$1.96\times10^{+20}$
Comparative Example	49	Si	Ge	6.5	–	–	B	0.3	$1.79\times10^{+20}$
	50	Si	Ge	6.5	–	–	P	1.0	$1.86\times10^{+20}$

【0046】

【Table 6】

	No.	Thermoelectric characteristics			
		Seebeck coefficient S(mV/K)	Electrical resistance ρ ($\Omega \cdot$ m)	Thermal conductivity κ (W/m · K)	Figure of merit (/K)
Example	41	0.36	8.40×10^{-6}	7.2	2.1×10^{-3}
	42	-0.36	7.20×10^{-6}	7.9	2.3×10^{-3}
	43	0.37	8.80×10^{-6}	6.9	2.3×10^{-3}
	44	-0.38	6.90×10^{-6}	7.6	2.8×10^{-3}
	45	0.34	8.80×10^{-5}	7.5	1.8×10^{-3}
	46	-0.35	7.30×10^{-6}	7.8	2.2×10^{-3}
	47	0.39	9.30×10^{-6}	7.4	2.2×10^{-3}
	48	-0.38	7.70×10^{-6}	7.9	2.4×10^{-3}
Comparative Example	49	0.32	7.90×10^{-6}	7.6	1.7×10^{-3}
	50	-0.34	8.20×10^{-6}	8.2	1.7×10^{-3}

【0047】

【Effects of the Invention】

As is clear from the examples, the thermoelectric conversion material of the present invention has a Seebeck coefficient of ± 2.0 to 4.0×10^{-4} V/K, which means that the thermal conductivity of this novel silicon-based thermoelectric conversion can be greatly decreased to 50 κ (W/m·K) or less and the Figure of merit markedly enhanced without decreasing the Seebeck coefficient originally had by the material.

【Brief Explanation of Drawings】

【Fig. 1】

Fig. 1 is a photograph taken by EPMA of the crystal structure of the thermoelectric conversion material of the present invention, where A shows the segregation of a germanuium added element (addition of 5 at%), and B shows the segregation of a phosphorus added element.

【Fig. 2】

Fig. 2 is a photograph taken by EPMA of the crystal structure of the thermoelectric conversion material of the present invention, where A shows the segregation of a germanuium added element (addition of 10 at%), and B shows the segregation of a phosphorus added element.

【Fig. 3】

Fig. 3 is a photograph taken by EPMA of the crystal structure of the thermoelectric conversion material of a

comparative example, where A shows the segregation of a germanuium added element (addition of 15 at%), and B shows the segregation of a phosphorus added element.

【Name of Document】 Summary

【Summary】

【Objects】 It is to provide a silicon-based thermoelectric conversion material and thermoelectric conversion element with which the thermal conductivity of a silicon-based thermoelectric conversion material can be greatly lowered without decreasing the Seebeck coefficient and electrical conductivity of the material, which affords a marked increase in the Figure of merit.

【Means for solving】 Adding carbon, germanium, or tin to a silicon-based thermoelectric conversion material allows the thermal conductivity to be greatly reduced without changing the carrier concentration in the silicon-based material. An added amount of 5 to 10 at% is ideal for lowering the thermal conductivity, and if an added element added to produce a p- or n-type semiconductor and a Group IV element are deposited at the grain boundary of polycrystalline silicon, the resulting p- or n-type semiconductor will have a carrier concentration of 10^{17} to 10^{21} (M/m^3) and a thermal conductivity of 50 W/m・K or less.

【Selected Figure】 None

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This is to certify that the annexed is a true copy of the following application as filed with this Office.

出願年月日 Date of Application:	１９９９年　８月３０日
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出願人 Applicant(s):	株式会社ＮＥＯＭＡＸ

２００４年　５月　７日

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